

On Some Characteristics of the Long and Short Spectral Lines

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(Plate IX.)

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1. *Introductory.*

In an electric arc the space from pole to pole, *i.e.*, the core of the arc is filled with the vapour of the substance under experiment. The temperature as well as the density in the core is very high as compared to those in the sides. If an image of the arc in the transverse position is thrown on the slit of an instrument for spectroscopic analysis, the spectrum obtained is that of a section of the arc normal to its length. In such a spectrum (see Plate IX, A) some lines stretch right across the core from side to side while others seem to originate from the core alone and thus appear to have a length much shorter than the former. These were designated as the *long* and *short* lines respectively by Lockyer.¹

Though this nomenclature is known to spectroscopists from a very long time no attempt at a systematic classification of the long and short lines with a view to trace their significant differentiating features seem to be on record. In the first

¹ Spectroscopy by E. C. C. Baly, p. 514, 1913; Phil. Trans., 164, 479 (1874).

instance the long and short lines of copper have been classified. On a scrutiny of these, a striking regularity has been observed, that if the relative orientation of the resultant l and s vectors in the initial and final states are compared, then those, for which the change in the orientation is large are invariably short lines; whereas those for which the orientation change is small come to the category of long lines. Besides these, transitions which indicate a change of the s vector, also come out as short lines; this, however, is not without exception.

Experiments have also been performed with the arc at reduced pressures (Plate IX, B) and the following interesting features have been noticed :—

1. Lines which are short in the arc at atmospheric pressure are further shortened in length.

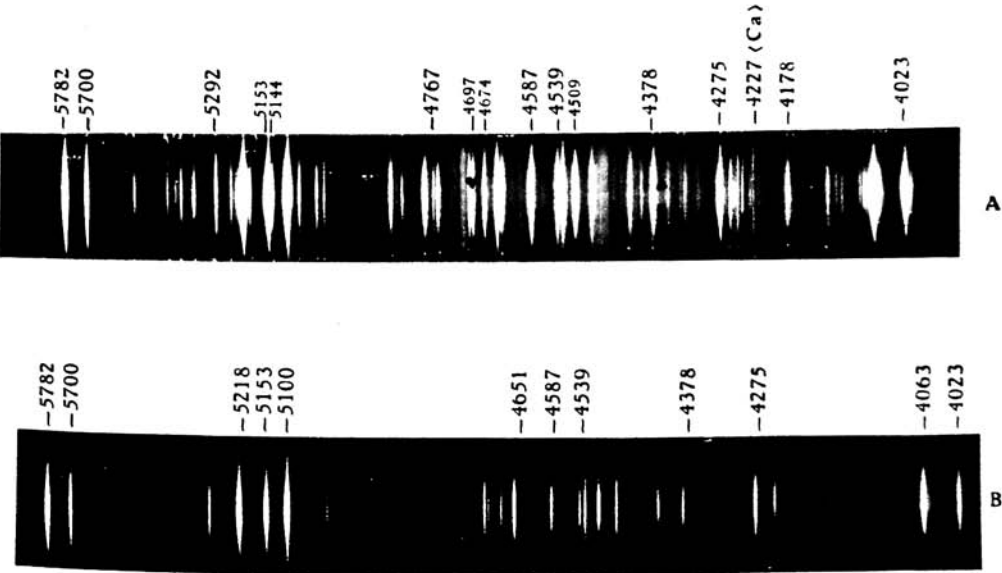
2. Lines which are ordinarily long and for which the orientation change is small but not zero appear as short lines.

3. Long lines for which the orientation change is zero generally persist as long lines even at comparatively low pressures.

Experiments are in progress with other metals, such as silver, zinc, iron, etc.

2. *Experimental.*

With the arc at atmospheric pressure, the arrangement consists in photographing the spectrum with the enlarged image of the arc in a horizontal position, focussed on the vertical slit of a large two-prism spectrograph with Littrow mounting giving a dispersion of 8 A. U. per mm. at $\lambda 4023$. The entire length of the slit (2 cm. long) was thus illuminated so that each part of the spectral image on the photographic plate, neglecting astigmatism, which is rather small in a prism spectrograph, may be regarded as corresponding to different points of the arcs along a normal to its length.



The chief difficulty in this experiment that had to be surmounted was to make the arc steady, which is essential in the present case to obtain any reliable results. This was done by the method adopted by H. Nagaoka and Y. Sugiura² and consisted in the introduction of a large capacity and self-inductance between the electrodes. A capacity of 3 micro-farad and a solenoid with a bundle of soft iron wires in the core were used.

For the best working, the current had also to be suitably adjusted. With copper arc, a current of about 5 amps. gave the best results.

Each time a photograph was taken, the ends of the rods of the metal were cut down into the form of a cone and this helped in keeping the arc still more steady.

In the visible region, high speed Ilford Panchromatic plates were used and an exposure of one and a half minutes was sufficient.

For experiments at low pressures, the electrodes were held horizontally, by some mechanical arrangement, inside a metal case provided with a small circular quartz window for letting out the light. The metal case was made air-tight by screwing on it a heavy lid provided with rubber pad round the four edges. The arc could be struck and the gap adjusted from outside by means of an electromagnetic arrangement. The pressure in the chamber was then reduced by a Cenco-Hyvac air pump.

3. *Experimental Results.*

Long and short lines of copper have been classified in three separate tables. Table I contains lines of the P—D and F—D combination. Transitions from various initial levels to a particular final level have been grouped together so as to show at a glance how the lengths vary as the orientations between the L

² Jap. Journ Phys., 8, 45 (1934).

and S vectors change. The orientation changes $\Delta \theta$ have been entered into the seventh column and has been calculated from the difference in the value of θ , i.e., the angle between the l and s vectors of the terms involved in the translation as obtained from the equation

$$\cos \theta = \frac{l^2 + S^2 - j^2}{2ls}.$$

The configurations of the atoms and the types of the various terms arising therefrom, as also their values have been obtained by reference to A. G. Shenstone, Phys. Rev., 28, 449 (1926), and Bacher and Goudsmit, "Atomic Energy States," pp. 175-179. First Edition, 1932.

TABLE I.

Final level.		Initial level.					
Configura- tion.	Symbol.	Configura- tion.	Symbol.	λ	Nature.	$\Delta \theta$ in degrees.	Remarks.
$3d^9 4s^2$.	$^2D_{\frac{3}{2}}$	$3d^{10} 4p$	$^2P^{\circ}_{\frac{1}{2}}$	5106	Long	0	Long at low pressures.
		$3d^9 4s 4p$	$^4P^{\circ}_{\frac{3}{2}}$	3594	Short	0	s changes
		$3d^9 4s 4p$	$^4P^{\circ}_{\frac{1}{2}}$	3456	Short	70	"
$3d^9 4s^2$.	$^2D_{\frac{5}{2}}$	$3d^{10} 4p$	$^2P^{\circ}_{\frac{3}{2}}$	5782	Long	0	Long at low pressures.
		"	$^2P^{\circ}_{\frac{1}{2}}$	5700		180	Shortened at low pressures.
		$3d^9 4s 4p$	$^4P^{\circ}_{\frac{1}{2}}$	3720	Short	70	s changes.
		"	$^4P^{\circ}_{\frac{3}{2}}$	3609	Short	0	"
		"	$^4F^{\circ}_{\frac{3}{2}}$	3530	Long	55	"
		"	$^4F^{\circ}_{\frac{1}{2}}$	3440	Short	0	"
$3d^{10} 4p$.	$^2P^{\circ}_{\frac{1}{2}}$	$3d^{10} 4d$	$^2D_{\frac{1}{2}}$	5153	Long	0	Long at low pressures.
		$3d^{10} 5d$	$^2D_{\frac{3}{2}}$	4023	Long	0	"

TABLE I.—(Contd.)

Final level.		Initial level.					
Configura- tion.	Symbol.	Configura- tion.	Symbol.	λ	Nature.	$\Delta\theta$ in degrees.	Remarks.
3d ⁹ 4s 4p.	² P° 1½	3d ¹⁰ 4d.	² D _{2½}	5218	Long	0	Long at low pressures.
		3d ¹⁰ 5d.	² D _{2½}	4063	Long	0	"
		3d ¹⁰ 6d.	² D _{2½}	3687	Long	0	"
	⁴ P° 2½	3d ⁹ 4s(3D)5s	⁴ D _{2½}	4178	Short	90	"
		"	⁴ D _{3½}	4275	Long	0	
		"	⁴ D _{1½}	4259	Short	62	
	⁴ P° 1½	"	⁴ D _½	4104	Short	110	Short at low pressures.
		"	⁴ D _{2½}	4378	Long	20	
		"	⁴ D _{1½}	4415	Short	48	
	⁴ P° ½	"	⁴ D _½	4248	Long	0	Long at low pressures.
		"	⁴ D _{3½}	4651	Long	0	
		"	⁴ D _{2½}	4587	Long	6	
	⁴ F° 4½	"	⁴ D _{3½}	4704	Short	84	Short at low pressures.
		"	⁴ D _{3½}	4797	Short	124	
		"	⁴ D _{2½}	4674	Short	34	
	⁴ F° 3½	"	⁴ D _{1½}	4539	Long	8	"
		"	⁴ D _{2½}	4842	Short	90	
		"	⁴ D _{1½}	4697	Short	48	
	⁴ F° 2½	"	⁴ D	4509	Long	0	"
		"	⁴ D _{3½}	5352	Long	180	
		"	⁴ D _{2½}	5201	Short	90	
	² F° 2½	"	⁴ D _{1½}	5034	Short	48	"
		"	⁴ D _{1½}				

Table II contains a set of short lines which do not follow the general rule laid down in the introductory section regarding the length of lines and their orientation changes. They however, all arise from a particular type of transition, viz., D°→D, P, F, G, whose peculiarities have been discussed in a subsequent section.

TABLE II.

Final Level.		Initial Level.			
Configura- tion.	Symbol.	Configuration.	Symbol.	λ	Nature.
$3d^9 4s 4p$	${}^4D^0_{3\frac{1}{2}}$	$3d^9 4s ({}^3D) 5s$	${}^4D_{\frac{1}{2}}$	5292	Short.
		"	4D	5144	"
		$3d^9 4s ({}^1D) 5s$	2D	4231	"
		$3d^9 4s ({}^3D_3) 4d$	2G_4	3655	"
		"	2D	3624	"
		"	2F	3620	"
	${}^4D^0_{3\frac{1}{2}}$	$3d 4s ({}^3D_3) 4s$	${}^4P_{2\frac{1}{2}}$	3613	"
		"	${}^4D_{3\frac{1}{2}}$	3602	"
		"	4F	3599	"
		$3d^9 4s ({}^3D_3) 4d$	${}^4G_{4\frac{1}{2}}$	3512	"
		"	${}^4F_{3\frac{1}{2}}$	3498	"
		$3d^9 4s ({}^3D_3) 5s$	${}^4D_{3\frac{1}{2}}$	5555	"
	${}^4D^0_{2\frac{1}{2}}$	"	${}^4D_{2\frac{1}{2}}$	5392	"
		$3d^9 4s ({}^1D) 5s$	${}^2D_{2\frac{1}{2}}$	4397	"
		"	${}^2D_{1\frac{1}{2}}$	4242	"
		$3d^9 4s ({}^3D_3) 4d$	${}^4S_{1\frac{1}{2}}$	3759	"
		"	${}^2D_{2\frac{1}{2}}$	3745	"
		"	${}^2F_{3\frac{1}{2}}$	3741	"
	${}^4D^0_{1\frac{1}{2}}$	"	${}^4P_{2\frac{1}{2}}$	3734	"
		$3d^9 4s ({}^3D_3) 4d$	${}^4D_{2\frac{1}{2}}$	3614	"
		"	${}^4F_{3\frac{1}{2}}$	8610	"
		$3d 4s ({}^3D_1) 4d$	${}^4G_{3\frac{1}{2}}$	3483	"
		"	${}^4G_{2\frac{1}{2}}$	3472	"
		$3d^9 4s ({}^3D) 5s$	${}^4D_{2\frac{1}{2}}$	5432	"
	${}^4D^0_{1\frac{1}{2}}$	"	${}^4D_{1\frac{1}{2}}$	5250	"
		"	${}^4D_{\frac{1}{2}}$	5016	"

TABLE II.—(Contd.)

Final Level.		Initial Level.		λ	Nature.
Configura- tion.	Symbol.	Configuration.	Symbol.		
$3d^9 4s 4p$	$^4D_{1\frac{1}{2}}$	$3d^9 4s(^1D)5s$	$^2D_{1\frac{1}{2}}$	4267	Short.
		$3d^9 4s(^3D_2)4d$	$^4D_{1\frac{1}{2}}$	3	"
	$^4D^0_{1\frac{1}{2}}$	$3d^9 4s(^3D_1)4d$	$^2S_{\frac{1}{2}}$	3500	"
		"	$^4G_{2\frac{1}{2}}$	3488	"
		"	$^4F_{2\frac{1}{2}}$	3475	"
	$^4D^0_{\frac{1}{2}}$	$3d^9 4s(^1D)5s$	$^2D_{1\frac{1}{2}}$	4336	"
		$3d^9 4s(^3D_1)4d$	$^2S_{\frac{1}{2}}$	35	"
		"	$^4F_{1\frac{1}{2}}$	"	"
	$^2D^0_{1\frac{1}{2}}$	$4d^9 4s(^3D)5s$	$^2D_{2\frac{1}{2}}$	5409	"
		$3d^9 4s(^1D)5s$	$^2D_{2\frac{1}{2}}$	4767	"
		$3d^9 4s(^3D_1)$	$^2S_{\frac{1}{2}}$	3712	"
	$^2D^0_{2\frac{1}{2}}$	$3d^9 4s(^3D)5s$	$^2D_{2\frac{1}{2}}$	5536	"
		$3d^9 4s(^1D)5s$	$^2D_{2\frac{1}{2}}$	4667	"
		$3d^9 4s(^3D_2)4d$	$^2D_{2\frac{1}{2}}$	4080	"
		"	$^2F_{3\frac{1}{2}}$	4075	"
		$3d^9 4s(^3D_1)4d$	$^4G_{3\frac{1}{2}}$	3772	"
		$3d^9 4s(^1D)4d$	$^2P_{1\frac{1}{2}}$	3487	"

Table III consists of lines corresponding to transitions involving an s level in which case the value of l being zero the angle between the l and s vectors becomes incomprehensible. It will be seen from this table that lines due to transition from energy levels higher than $3d^{10} 6s$ are short. Below this all lines are long.

TABLE III.

Final Level.		Initial Level.		λ	Nature.
Configura- tion.	Symbol.	Configuration.	Symbol.		
$3d^{10}4s$	$^2S_{\frac{1}{2}}$	$3d^{10}4p$	$^2P^0_{\frac{1}{2}}$	3274	Long.
		$3d^{10}4p$	$^2P^0_{\frac{3}{2}}$	3248	"
$3d^{10}4p$	$^2P^0_{\frac{1}{2}}$	$3d^{10}6s$	$^2S_{\frac{1}{2}}$	4481	"
		$3d^{10}7s$	$^2S_{\frac{1}{2}}$	3825	Short.
		$3d^{10}8s$	$^2S_{\frac{1}{2}}$	3566	"
		$3d^{10}6s$	$^2S_{\frac{3}{2}}$	4530	Long.
	$^2P_{\frac{1}{2}}$	$3d^{10}7s$	$^2S_{\frac{3}{2}}$	3861	Short.
$3d^94s4p$	$^4D^0_{\frac{3}{2}}$	$3d^94s(^3D_3)4d$	$^4S_{\frac{1}{2}}$	3759	"
	$^4D^0_{\frac{1}{2}}$	$3d^94s(^3D_1)4d$	$^2S_{\frac{1}{2}}$	3500	"
	$^4D^0_{\frac{5}{2}}$	"	$^2S_{\frac{3}{2}}$	3546	"
	$^2F^0_{\frac{3}{2}}$	$3d^94s(^3D_3)4d$	$^4S_{\frac{3}{2}}$	3665	"
	$^2P^0_{\frac{1}{2}}$	$3d^94s(^3D_1)4d$	$^2S_{\frac{3}{2}}$	3671	"
	$^2D^0_{\frac{1}{2}}$	$3d^94s(^3D_1)4d$	$^2S_{\frac{5}{2}}$	3712	"

Besides the lines tabulated in the above three tables, there are other lines which arise out of transitions between levels of very high energy content. They come out as comparatively weak and short lines, and this is what one would expect, remembering the fact that according to the laws of probability, number of such atoms is very small.

4. Observations.

From Table I it is clear that lines for which the change in the orientation is large are short in the arc at atmospheric pressure. With a reduction in pressure they either disappear or

are considerably reduced in length. Whereas the lines for which $\Delta\theta$ is small but not negligible and which have been classed as long lines, under reduced pressure appear as short lines, the lines at $\lambda\lambda$ 4587, 4539, 4378 being examples in point; but lines for which $\Delta\theta$ is zero remain fairly long even at a comparatively low pressure. As examples, the lines at $\lambda\lambda$ 5782, 5218, 5153, 5106, 4651, 4275, 4063 may be mentioned. These lines remain unaffected in length even at a pressure of 30cm. (Plate IX, B) and all these lines have their orientation change equal to zero. The lines at $\lambda\lambda$ 4509, 4248 and 4023 are only slightly diminished in length at this pressure. It would thus mean that the *a priori* probability of a particular transition is, to a great extent, determined by $\Delta\theta$, being larger the smaller the value of $\Delta\theta$; so that in the cases of transitions involving $\Delta\theta=0$, a very small quantity of vapour is sufficient to produce the line, hence it appears long even at a reduced pressure. Incidentally it may be pointed out that the persistent lines of De Gramont also belong to this category. Some of the lines, however, appear not to follow this rule, and as in their cases there is a spin change, their shortening may be due to the latter cause. The line at λ 3530 seems to be an exception. A few words might be necessary for the line at λ 5700, one of the most heavy lines in the arc spectrum of copper. The length of this line lies intermediate between those of the long and short lines so that its classification in the present system might seem to be uncertain. But the question is at once settled from its behaviour at low pressure where it is considerably shortened in length like all other short lines. Thus, it should rather be called a short line than a long one.

In the case of D° transitions, lines of which are all short, attention may be drawn to an interesting feature, *viz.*, D° type is obtained as a result of synthesis of l vectors of orbits which are apparently not parallel but inclined to one another. For instance the configuration $3d^9(4s4p)$ gives rise to doublet and quartet terms of $F^{\circ}D^{\circ}P^{\circ}$ type. Now, of them F° ($l=3$) and

$P^\circ (l=1)$ are obtained by the sum and difference of the l value of $3d^0$ ($\equiv 3d^1$) and $3p$ orbits, $4s$ not contributing at all ($\because l=0$). This, *a priori*, means that the l vectors are either parallel or anti-parallel, whereas in the type $D^\circ (l=2)$ they must be inclined. It may be suggested that this latter type of synthesis is not generally favoured and therefore comparatively larger quantity of vapour would be necessary for their production.

As early as 1874 Lockyer³ observed, and this has been confirmed in case of the present experiment, that many weak lines are longer than some very strong lines and among lines of equal intensity some are considerably longer than the others. They, however correspond to cases where there is a little or no change in the orientation of the l and s vectors. Some of these lines have been selected and their lengths have been measured by

TABLE IV.

λ	Designation.	Intensity.	Length in mm.	$\Delta\theta$	Remarks.
4275	$^4P_{2\frac{1}{2}} - ^4D_{3\frac{1}{2}}$	6	17.4	0°	
4378	$^4P_{1\frac{1}{2}} - ^4D_{2\frac{1}{2}}$	6u	15.2	20°	
4674	$^4F_{2\frac{1}{2}} - ^4D_{2\frac{1}{2}}$	6u	14.2	84°	
4509	$^4F_{1\frac{1}{2}} - ^4D_{\frac{1}{2}}$	4	16.7	0°	
4539	$^4F_{2\frac{1}{2}} - ^3D_{1\frac{1}{2}}$	4u	16.7	8°	
4697	$^4F_{1\frac{1}{2}} - ^4D_{1\frac{1}{2}}$	4u	13.6	48°	
4178	$^4P_{2\frac{1}{2}} - ^4D_{2\frac{1}{2}}$	4u	12.2	90°	
5292	$^4D_{3\frac{1}{2}} - ^4D_{3\frac{1}{2}}$	4	14.0	0°	D° combination.
4767	$^3D_{1\frac{1}{2}} - ^3D_{2\frac{1}{2}}$	2u	10.0	180°	"
5144	$^4D_{3\frac{1}{2}} - ^4D_{2\frac{1}{2}}$	1u	11.5	90°	"

³ See Spectroscopy by E. C. C. Baly, p. 514, 1918 and reference given there.

means of a low power travelling telescope. Such lines have been collected in Table IV, which shows their lengths and intensities⁴ as also their $\Delta\theta$ values.

From the above table it is apparent that there is no very close relation between lengths of lines and their intensities. The lengths in these cases are rather consistent with the generalisations laid down before.

The fact that the length of a line is not always regulated by its intensity is very clearly brought out by the line at λ 4226.79 [$4s^2(^1S) - 4s4p(^1P_1^o)$] due to calcium as impurity (see plate IX, A). Although weak, this line stretches from edge to edge with about undiminished intensity, whereas many stronger lines of copper appear much shorter than this.

From the above results it is evident that near the edge of the flame of the arc, some weak lines are present although some equally intense lines or even some comparatively stronger lines, are absent at the point. A similar phenomenon was observed by M. Kimura and G. Nakamura.⁵ They observed that in the spectrum of the light emitted from the neighbourhood of the salt cathode of copper in a discharge tube some heavier lines in the arc and spark spectra of copper such as $\lambda\lambda$ 5700, 4587, etc., are absent. It is interesting to note that if in these cases also, the synthesis of the l and s vectors taking part in the scheme of level transition be scrutinised, then it is seen that these lines correspond to cases where there is a change in the relative orientation of the l and s vectors. The results obtained by Kimura and Nakamura have been collected in Table V. The 2nd, 6th and the 7th columns have been introduced by the writers.

Thus the cathode spectrum of the CuCl_2 discharge tube resembles that of a vacuum arc of copper.

⁴ Intensities have been taken from Shenstone's paper : *Phys. Rev.*, 26, 449 (1926), *Jap. Journ. Phys.*, 3, 99 (1924).

TABLE V.

λ	Designation.	Arc.	Intensity Spark.	Cathode space of CuCl_2 .	$\Delta\theta$	Lines as they appear in the low pressure arc.
5782	$^3\text{D}_{1\frac{1}{2}} - ^3\text{P}_{\frac{1}{2}}$	50	10	3	0°	Long.
5700	$^3\text{D}_{1\frac{1}{2}} - ^3\text{P}_{1\frac{1}{2}}$	30	8	0	180°	Short.
5220	$^3\text{P}_{1\frac{1}{2}} - ^3\text{D}_{1\frac{1}{2}}$	20	8	0	180°	Short.
5918	$^3\text{P}_{1\frac{1}{2}} - ^3\text{D}_{2\frac{1}{2}}$	200	200	10	0°	Long.
5153	$^3\text{P}_{\frac{1}{2}} - ^3\text{D}_{1\frac{1}{2}}$	100	100	5	0°	Long.
5106	$^3\text{D}_{2\frac{1}{2}} - ^3\text{P}_{1\frac{1}{2}}$	50	20	9	0°	Long.
4704	$^4\text{F}_{3\frac{1}{2}} - ^4\text{D}_{3\frac{1}{2}}$	8	2	0	84°	Short.
4651	$^4\text{F}_{4\frac{1}{2}} - ^4\text{D}_{3\frac{1}{2}}$	20	10	8	3°	Long.
4587	$^4\text{F}_{3\frac{1}{2}} - ^3\text{D}_{2\frac{1}{2}}$	20	20	0	0°	Short.